

What is claimed is:

- 1 1. A method of stimulating a subterranean formation penetrated by a well
2 comprising the steps of:
 - 3 (a) introducing into the formation an aqueous treatment fluid
4 containing a hydrophobically-modified RPM; and
 - 5 (b) introducing an acidizing treatment fluid into the formation.
- 1 2. The method of Claim 1, wherein the hydrophobically-modified RPM is
2 the reaction product of a hydrophilic polymer and a hydrophobic compound that are
3 capable of reacting with each other.
- 1 3. The method of Claim 2, wherein the hydrophilic polymer is a polymer
2 containing reactive amino groups in the polymer backbone or as pendant groups, which
3 are capable of reacting with a hydrophobic alkyl halide compound.
- 1 4. The method of Claim 3, wherein the hydrophilic polymer is a homo-
2 polymer, co-polymer, or ter-polymer.
- 1 5. The method of Claim 3, wherein the hydrophilic polymer contains dialkyl
2 amino pendant groups.
- 1 6. The method of Claim 3, wherein the hydrophilic polymer contains a
2 dimethyl amino pendant group and contains at least one monomer selected from the
3 group consisting of dimethylaminoethyl methacrylate and dimethylaminopropyl
4 methacrylamide.
- 1 7. The method of Claim 3, wherein the hydrophilic polymer is an alkyl
2 acrylate polymer.

1 8. The method of Claim 3, wherein the hydrophilic polymer is selected from
2 the group consisting of polyethyleneimine, polyvinylamine, poly(vinylamine/vinyl
3 alcohol), chitosan, and polylysine.

1 9. The method of Claim 3, wherein the hydrophilic polymer is selected from
2 the group consisting of polydimethylaminoethyl methacrylate, polydimethylaminopropyl
3 methacrylamide, poly(acrylamide/dimethylaminoethyl methacrylate),
4 poly(acrylic acid/dimethylaminoethyl methacrylate),
5 poly(methacrylic acid/dimethylaminoethyl methacrylate),
6 poly(acrylamide/dimethylaminopropyl methacrylamide),
7 poly(acrylic acid/dimethylaminopropyl methacrylamide), and
8 poly(methacrylic acid/dimethylaminopropyl methacrylamide).

1 10. The method of Claim 3, wherein the hydrophilic polymer is selected from
2 the group consisting of polydimethylaminoethyl methacrylate and
3 polydimethylaminopropyl methacrylamide.

1 11. The method of Claim 3, wherein the hydrophobic alkyl halide compound
2 is an alkyl halide having an alkyl chain length of 6 to 22 carbons.

1 12. The method of Claim 11, wherein the hydrophobic alkyl halide compound
2 is hexadecyl bromide.

1 13. The method of Claim 3, wherein the hydrophobically-modified RPM is a
2 homopolymer of DMAEMA quaternized with hexadecyl bromide.

1 14. The method of Claim 3, wherein the hydrophobically-modified RPM is
2 dissolved in an aqueous solution and then injected into the formation.

1 15. The method of Claim 3, wherein the hydrophobically-modified RPM is
2 introduced into the formation by mixing the hydrophilic polymer and the hydrophobic

3 alkyl halide compound in the aqueous treatment fluid in situ during the well stimulation
4 process.

1 16. The method of Claim 15, wherein the hydrophilic polymer comprises from
2 about 0.1% to about 2% by weight of the aqueous treatment fluid and the hydrophobic
3 compound comprises from about 0.01% to about 1% by weight of the aqueous treatment
4 fluid.

1 17. The method of Claim 15, wherein the hydrophilic polymer comprises
2 about 0.2% to about 1.5% by weight of the aqueous treatment fluid and the hydrophobic
3 compound comprises from about 0.02% to about 0.5% by weight of the aqueous
4 treatment fluid.

1 18. The method of Claim 15, wherein the aqueous treatment fluid further
2 comprises a surfactant to promote the dissolution of the hydrophobic compound in
3 aqueous treatment fluid.

1 19. The method of Claim 18, wherein the surfactant is selected from the group
2 consisting of alkyl ammonium surfactants, betaines, alkyl ether sulfates, alkyl ether
3 sulfonates, and ethoxylated alcohols.

1 20. The method of Claim 18, wherein the surfactant is present within the
2 aqueous solution in amounts ranging from about 0.1 % to about 2 % by weight.

1 21. The method of Claim 3, wherein the hydrophobically-modified RPM is a
2 polymeric material having molecular weights in the range of about 250,000 to about
3 3,000,000.

1 22. The method of Claim 3, wherein the hydrophobically-modified RPM is
2 present in the aqueous treatment fluid in a concentration from about 0.02% to about 3%
3 by weight.

1 23. The method of Claim 3, wherein the hydrophobically-modified RPM is
2 present in the aqueous treatment fluid in a concentration from about 0.05% to about 1%
3 by weight.

1 24. The method of Claim 3, wherein the aqueous treatment fluid is at a pH of
2 between about 4 and about 8.

1 25. The method of Claim 1, wherein the hydrophobically-modified RPM
2 polymer is prepared from the polymerization reaction of at least one hydrophilic
3 monomer and at least one hydrophobically-modified hydrophilic monomer.

1 26. The method of Claim 25, wherein the hydrophilic monomer is selected
2 from the group consisting of acrylamide, 2-acrylamido-2-methyl propane sulfonic acid,
3 N,N-dimethylacrylamide, vinyl pyrrolidone, dimethylaminoethyl methacrylate, acrylic
4 acid, dimethylaminopropylmethacrylamide, vinyl amine, vinyl acetate,
5 trimethylammoniummethyl methacrylate chloride, methacrylamide, and hydroxyethyl
6 acrylate.

1 27. The method of Claim 25, wherein the hydrophobically-modified
2 hydrophilic monomer is selected from the group consisting of alkyl acrylates, alkyl
3 methacrylates, alkyl acrylamides and alkyl methacrylamides wherein the alkyl radicals
4 have from about 4 to about 22 carbon atoms, alkyl dimethylammoniummethyl methacrylate
5 bromide, alkyl dimethylammoniummethyl methacrylate chloride and alkyl
6 dimethylammoniummethyl methacrylate iodide wherein the alkyl radicals have from about
7 6 to about 22 carbon atoms and alkyl dimethylammoniumpropyl methacrylamide
8 bromide, alkyl dimethylammonium propylmethacrylamide chloride, and alkyl
9 dimethylammoniumpropyl methacrylamide iodide, wherein the alkyl groups have from
10 about 4 to about 22 carbon atoms.

1 28. The method of Claim 25, wherein hydrophobically-modified RPM is a
2 polymeric material having molecular weights in the range of from about 250,000 to about
3 3,000,000.

1 29. The method of Claim 25, wherein hydrophobically-modified RPM has
2 mole ratios of the hydrophilic monomer(s) to the hydrophobically-modified hydrophilic
3 monomer(s) in the range of from about 99.98:0.02 to about 90:10.

1 30. The method of Claim 25, wherein hydrophobically-modified RPM is a
2 dimethylaminoethyl methacrylate/hexadecyldimethylammoniummethyl methacrylate
3 bromide copolymer having a mole ratio of hydrophilic monomer to hydrophobically-
4 modified hydrophilic monomer of 95:5.

1 31. The method of Claim 3 or Claim 25, wherein hydrophobically-modified
2 RPM is capable of being dissolved in water at a concentration of at least 0.2% by weight
3 and is capable of imparting a resistance factor for water of greater than a resistance factor
4 for hydrocarbon as measured across a sandstone core of about 2.5 cm diameter by about
5 14 cm long and having an initial permeability to brine of about 1,000 md.

1 32. The method of Claim 31, wherein when the hydrophobically-modified
2 RPM is tested at the concentration of 0.2% by weight, it is capable of imparting a
3 resistance factor for water of greater than about 3 and a resistance factor for hydrocarbon
4 of less than about 2.

1 33. The method of Claim 3 or 25, wherein the hydrophobically-modified RPM
2 is introduced into the formation prior to the acidizing treatment fluid.

1 34. The method of Claim 3 or 25, further comprising the step of shutting in
2 the well after introducing the polymeric material into the well.

1 35. A method of acidizing a subterranean formation penetrated by a well
2 comprising the steps of:
3 (a) introducing into the formation an aqueous treatment fluid containing from
4 about 0.02% to about 3% by weight of a water-soluble, hydrophobically-modified RPM
5 that is the reaction product of a hydrophilic polymer and a hydrophobic compound that
6 are capable of reacting with each other, wherein the hydrophilic polymer is a polymer
7 containing reactive amino groups in the polymer backbone or as pendant groups, which
8 are capable of reacting with a hydrophobic alkyl halide compound having an alkyl chain
9 length of 6 to 22 carbons; and
10 (b) introducing an acidizing treatment fluid into the formation.

1 36. The method of Claim 35, wherein the hydrophobically-modified RPM is
2 dissolved in an aqueous solution and then injected into the formation.

1 37. The method of Claim 3, wherein the hydrophobically-modified RPM is
2 introduced into the formation by mixing the hydrophilic polymer and the hydrophobic
3 alkyl halide compound in the aqueous treatment fluid in situ during the well stimulation
4 process.

1 38. A method of acidizing a subterranean formation penetrated by a well
2 comprising the steps of:
3 (a) introducing into the formation an aqueous treatment fluid containing from
4 about 0.02% to about 3% by weight of a water-soluble, hydrophobically-modified RPM
5 that is prepared from the polymerization reaction of at least one hydrophilic monomer
6 and at least one hydrophobically-modified hydrophilic monomer; and
7 (b) introducing an acidizing treatment fluid into the formation.

1 39. The method of Claim 38, wherein the hydrophobically-modified RPM is
2 dissolved in an aqueous solution and then injected into the formation.

1 40. The method of Claim 38, wherein the hydrophobically-modified RPM is
2 introduced into the formation by mixing the hydrophilic polymer and the hydrophobic
3 alkyl halide compound in the aqueous treatment fluid in situ during the well stimulation
4 process.